THE SYNTHESIS AND CHARACTERIZATION OF PHOSPHONIC ACIDS FOR THE SURFACE MODIFICATION STUDY ON INDIUM TIN OXIDE

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SUMMARY

The synthesis and characterization of some phosphonic acids as well as the modification of indium tin oxide (ITO) substrates using these phosphonic acids are presented in this thesis. Phosphonic acids have been known to bind strongly to the surface of a number of metal oxides. ITO substrates were reported to be modified with a variety of surface modifiers. Herein the ITO substrates were modified with the chosen phosphonic acids with different functional groups in order to tune the work function and compare the work function changes with the functional group properties.

CHAPTER 1

INTRODUCTION

The content of this thesis focuses on surface modification of conducting oxides for organic electronics devices, i.e. changing electrode properties by modification of the electrode surfaces with phosphonic acids. Specifically the purpose is to investigate the evolution of the work function changes of indium tin oxide (ITO) upon modification of its surface using phosphonic acids with different head functional groups. This thesis will discuss the design, synthesis and characterization of the surface modifiers – phosphonic acids, characterization of the modified ITO surfaces and the property changes of the surfaces.

1.1 Brief Introduction to Organic Electronics

"Organic electronics" represents a branch of study that includes both science and engineering that attempts to exploit the use of organic materials in combination with inorganic materials to be used as one or several active components in electronic and optical devices such as organic light emitting diodes (OLED), organic solar cells (OSC), organic thin film transistors (OFET), organic magnets (OM) for spintronics etc. This field has drawn substantial interests from the science and engineering community as well as considerable research investment. Because of this, technologies based upon organic materials have been advancing rapidly over the last 30 years or so since the discovery of the conductivity of polyacetylene,[1,2] before which the possible application of organic molecules in field of molecular electronics[3,4] has been realized by researchers in the mid 70's.

Organic electronic devices have several potential advantages with respect to some inorganic counterparts such as the fact that they can be lightweight, flexible, in some cases processed from solution. As a consequence they have promise to be manufactured inexpensively, to achieve excellent device performance by some metrics. However, currently for most applications the conventional inorganic materials still outperform organic materials when judged by parameters such as higher overall efficiency, longer lifetime etc. which are the driving forces for the chemistry and materials science community to continually explore the solution processible, less expensive and stable organic materials that have better device performance.

The organic materials used in the organic electronic devices are typically conjugated organic molecules and polymers, which are semiconducting in their undoped state. So the use of organic materials in the devices makes it possible to modify the electronic and optical properties of the device by tailoring the chemical structure of the organic molecule.

Some areas of research in this field include exploration of novel semiconducting materials, surface modification (which can be used for matching the charge carrying energy level of the organic material and Fermi level of electrode surface), and optimization of device performance to name a few. The contents of this thesis pertain to the surface modification part of this research.

1.2 Processes in Devices and Interface Properties

In all of the organic electronics devices mentioned above, the common structure of devices includes several layers on top of each other. The charges flow through the multilayers and so the transport of charges across the electrode/active semiconducting layer (including inorganic/organic and organic/organic) interfaces play a key role for device performance. Since the energy barriers for injection or extraction of charge

carriers into and out of an active organic layer need to be minimized, so in order to achieve high efficiency proper matching of the electronic energy levels between different active layers is very important.[5] So considerable effort has been devoted to optimize energy level alignment between the different materials and the understanding of these interfaces is therefore crucial.[6-9]

As the energy level matching between two different layers closely relates to the device operation processes of OLEDs and OSCs, the basic device operation processes of the above two devices will be discussed as follows. Generally these two devices have similar basic constituents in their structure, they both contain anodes, cathodes and semiconducting layers for hole and electron transport, which usually include an organic hole transporting layer (HTL) and electron transporting layer (ETL). Though there exist many other device designs and architectures which include more layers for various reasons. For simplicity only the most basic one will be discussed here.

For OPV the process of light absorption and conversion to current can be described using five steps: 1) photon absorption, 2) exciton formation and diffusion, 3) exciton dissociation and charge separation, 4) charge transport to both electrodes, 5) charge collection at both electrodes.

In OLED the process is reversed, so that light is emitted by applying a voltage to the device: 1) charge injection by application of voltage between the electrodes, 2) charge transport in the corresponding layers, 3) charge migration and charge build up at the organic heterojunction, 4) charge recombination and exciton formation, 5) exciton decay and light emission.

As described above, organic electronic devices typically contain a number of layers (which have different work functions). Since many of the key processes such as charge injection in OLED, and charge separation in OSC take place at the interfaces between the materials, thus the charge transfer process across these interfaces and

fundamental physical and chemical processes behind need to be fully understood in order to improve device performance.

In the following sections, the most important parameters regarding surface and interfacial properties will be discussed in detail.

1.2.1 Basic Concepts and Definitions

In organic electronic devices such as OLED, the most simple structure consists of a high work function hole injecting or collecting anode and a low work function electron injecting or collecting electrode with the active organic layers in between.[10] At least two different types of interfaces are present and have direct influence on the device performance through the energy alignment of the different materials. Figure1.1 illustrates the most simplified single-layer OLED device and the corresponding energy level diagram of the OLED operation. Important parameters that are relevant to device operation include ionization potential (IP) of the organic material, electron affinity (EA) of the organic material, work functions (WF) of anode (Φ_{anode}) and cathode ($\Phi_{cathode}$), and the electron and hole-injection barriers, φ_e and φ_h respectively. The work function is defined as the energy required for removing an electron from the Fermi level (E_F) of a material and putting it at rest beyond the electronic influence of the materials (i.e. at the so called vacuum level). IP of a material corresponds to the difference between E_{vac} and its Highest Occupied Molecular Orbital (HOMO) and EA corresponds to the difference between E_{vac} and its Lowest Unoccupied Molecular Orbital (LUMO). The hole-injection barrier φ_h is the difference between Fermi level (E_F) of the anode and HOMO of the organic material. Similarly the electron-injection barrier φ_e is the difference between Fermi level (E_F) of the cathode and LUMO of the organic material.

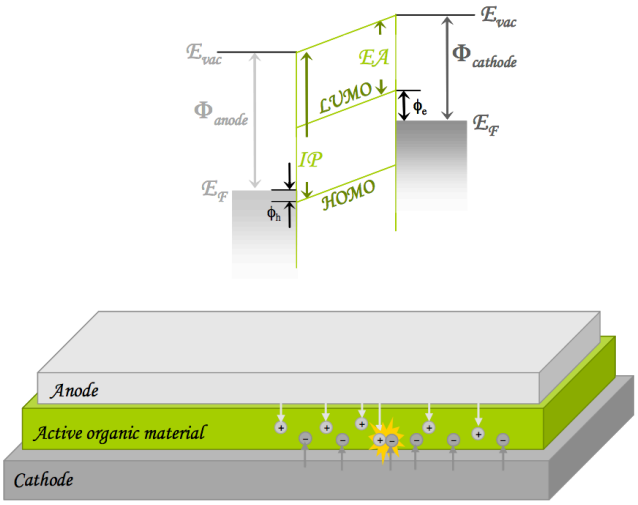

Figure1.1 Schematic picture of a simplified OLED structure and related energy levels.[16]

At the interface of the electrode and active organic material, one important parameter is the energy alignment between different layers. That is to say the electron and hole-injection barriers need to be minimized in order to optimize the device performance. To do so, two things can be considered: 1) change the IP and EA of the organic material; 2) change the work function of the electrode. With a specific organic material, it may not be optimal to change its structure to it because it will modify all the other desired properties of the molecule as well. Hence the surface modification of the electrode to change the work function of the electrode is an alternative approach to be considered.

It has been widely known that the work function of a clean surface can be modified by introducing an interface dipole $D_{interface}$[11, 12, 13]. This can be used to optimize the alignment of energy levels at interfaces to decrease the charge injection barriers in organic-based devices.

When a monolayer of organic molecules is deposited onto the electrode surface, the magnitude of the interface dipole $D_{interface}$ can be determined by the change of the

surface work function[14]. An interface dipole with its positive end pointing towards the organic layer and its negative end pointing towards the electrode decreases the work function of the electrode thereby decreasing the energy difference between the LUMO of the organic layer and the Fermi level of the electrode.[15] As a result, the electron injection energy barrier is reduced. Similarly the hole injection barrier can be reduced by reversing the above interface dipole. Thus, a work function decrease (increase) is associated with a higher efficiency of electron (hole) injection.

The interface dipole is usually considered to depend mostly on three contributions:[16, 17]

1) ΔD_{surf}, a decrease of the electron density tail (push-back effect) on the electrode surface;[18, 19]

2) D_{chem}, a chemical dipole due to the charge transfer between the electrode surface and the molecule;[20, 21]

3) D_{mol}, an intrinsic dipole on the surface normal of the attached molecule.[5, 22] The interface dipole (or the work function change) can thus be expressed as a function of the three contributions ("e" represents an charge of a electron):

$$eD_{interface} = f(e\Delta D_{surf} , eD_{chem} , eD_{mol}) \propto \Delta\Phi .$$

The above three factors will be explained further in the following sections but it can be kept in mind already that the contribution due to shrinking of the electron density tail on the electrode surface always reduces the work function of the bare surface and is a contribution that is always present when adsorbing any species on the surface. In other words, this contribution (ΔD_{surf}) is always present whether both of the other two contributions apply or not. The second and third contributions, chemical dipole and intrinsic molecular dipole can introduce work function changes in both directions depending on the direction of charge transfer and intrinsic dipole of the attached molecule respectively.

1.2.2 Surface Dipole

An important parameters in surface science related to organic electronics is the work function (Φ) of the materials. Since the Fermi level is a fixed energy level of the surface, the difference in work function is caused by the different potential felt by the electron when passing by the surface. (The measured work function can however be different for a single crystal material depending on from which plane of the crystal electrons are removed.) At the surfaces the negatively charged electron cloud into the vacuum appears at the surface, leaving the surface side positively charged while the vacuum side is negatively charge, then a surface dipole is created (This phenomenon is described with more detail in the Jellium model[23]).

1.2.3 Charge Transfer Dipole

In the situation where the molecule is chemically bounded to the surface the surface – molecule bond is formed between the attached molecule and the surface at the atomic level. Depending on the type of the interaction, both ionic (charge transfer) and covalent (mixing of molecular orbitals) bond can be formed. Thus an induced change in the work function of a surface can be seen upon deposition of the molecules on the surface.

1.2.4 Intrinsic Molecular Dipole

When dipolar molecules are attached onto a surface, the work function of the combined molecule-surface layers will be affected by the net molecular dipole to the surface normal. Additionally, the chemical interaction that occur between the surface and the adsorbed molecule also contributes to the work function changes as the charge transfer dipole described above.

Based on the desire to impact the molecular factors mentioned above, one of the most common ways to change the work function is to use the so-called self-assembled monolayers (SAMs) of molecules with intrinsic dipole moment along the molecule. Since SAMs are usually packed in a high degree of structural order, the individual molecular dipole moments are aligned in the same direction and sum up to give a large shift in terms of work function. Hence the magnitude of the work function change can be tuned chemically by changing the polarity of the molecule. This term will be discussed in more detail in the following section.

1.2.5 Background on Self–Assembled Monolayers (SAMs)

The term self–assembled monolayer (SAM) has been widely used in the literature during the recent twenty years especially in nanotechnology. Readers can find quite a few excellent comprehensive reviews[24-28] in the literature in organic electronics field. Back in 1991, Ulman defined a SAM as a monomolecular film of a surfactant formed spontaneously on a substrate upon exposure to a surfactant solution[29]. In 2005, Love *et al.* described SAMs as organic assemblies formed by the adsorption of molecular constituents from solution or the gas phase onto the surface of solids or in regular arrays on the surface of liquids (in the case of mercury and probably other liquid metals and alloys); the adsorbates organize spontaneously (and sometimes epitaxially) into crystalline (or semicrystalline) structures[25]. This description includes two important factors: first, the layer formed on the surface is a monolayer. Secondly, the molecules in that monolayer have self-assembly behavior, but this term has been used in the literature to describe all types of organic monolayers systems without precision since the introduction of the concept.

The introduction of SAMs onto the surface can be used in many fields to tune various properties of the surface such as modification of wetting properties, corrosion

protection, modification of work function in organic electronics, chemical sensing, nanolithography, etc.[25] This thesis only focuses on the modification of work function upon the deposition of phosphonic acids onto metal oxide surfaces. It has been shown that oftentimes hydrogen–bonded multilayers of phosphonic acids are first deposited on a given surface, only to become monomolecular after heating and/or washing.[30-32] Additionally, whether or not the phosphonic acids is "self–assembled" on the surface has not been investigated in this thesis, consequently, the use of the term SAM is not fully justified in the present case and will not be used to describe the system herein. However, based on the property change of the surfaces and modification steps, we can still argue that the interface system under consideration very much resembles a SAM.

1.2.6 Work Function Tuning

Based on the factors discussed in the previous section and the relationship between surface dipole and work function, the contributions to work function change will be discussed here.

When a monolayer of molecules is deposited on a surface (either metal or conducting metal oxide), in addition to the initial surface dipole two factors can play important roles in terms of modifying the surface thus changing the work function of the surface: charge transfer dipole and intrinsic molecular dipole. Also the molecular packing on the surface will influence the net change of the dipole moment. Similar to dipole moment, there are three corresponding factors will have impact for the work function change on the surface:[28,33]

1) The potential step (ΔV) across the introduced molecular layer (relates to the intrinsic molecular dipole and percent coverage of the unit area of the surface);

2) Bond dipole (BD) upon metal-SAM bond formation (relates to the surface dipole and charge transfer dipole, includes the decrease in metal surface dipole – "pillow"

effect, which describes the reduction of the electrode work function due to the adsorbed molecules);

3) Geometry rearrangement energy of the surface, Δ (geom).

So the contributions to the work function change can be summarized as a function of the three components in the following equation: $\Delta\Phi = f(BD + \Delta V + \Delta(geom))$[49]

In this thesis, the monolayer of molecule is introduced onto the electrode surface. Because the interface dipole will be changed upon deposition, the work function of the electrode is changed accordingly. The surface modifiers used in my experiments are benzyl and phenyl phosphonic acids with different dead groups (namely nitro, cyano, fluoro and hydrogen) at the *para* position. By looking at the relationship between work function change and dipole moment/Hammett parameter, we can gain insights on structure – property correlations. Details of the work will be presented in the next chapters.

1.3 Phosphonate and Phosphonic Acid

Phosphonates are species of organic compounds containing R'-$PO(OR)_2$ groups (where R, R' = alkyl, aryl); the structure of phosphonates compound includes a tetra coordinate phosphorus atom in the +5 oxidation state that is connected to two alkoxy groups with P-O single bond and a formally double–bonded oxygen (known as a phosphoryl group). The fourth group and the R of the two alkoxy groups can be a variety of species, so changes can be made chemically. Phosphonates are often used as the precursors to prepare the corresponding phosphonic acids. Phosphonates are often viscous oils at room temperature, well soluble in common organic solvents and stable in air at high temperature.

Phosphonic acids are compounds which contain R-$PO(OH)_2$ groups (where R=alkyl, aryl), they have similar structure with phosphonate except the central

phosphorus atom is bound to two hydroxyl groups. Variety can also be made possible chemically. Phosphonic acids are usually solids at room temperature and stable under harsh conditions such as high temperature over long periods of time. Phosphonic acids tend to be soluble in polar solvents, such as dimethylsulfoxide (DMSO) and ethanol. They are sometimes soluble in water, however this is highly dependent on the R–group attached to the phosphonic acid.

1.3.1 Why use Phosphonic Acids Rather Than Other Molecules for Metal Oxide Surface Modification

It has been shown that there are several different species of molecules that can be used to bind to metal oxides. The possible binding groups include alcohols, carboxylic acids, silanes, sulfonic acids, phosphinic acids and phosphonic acids[35]. We will discuss the ones that have been studied more extensively: silanes, carboxylic acids and phosphonic acids.

Alkoxy and halogenated silanes are among one of the most widely used moieties that bind to metal oxides in particular silica. The typical molecule has up to three covalent bonds that potentially can be bounded to the surface of metal oxides. They have been used to form very dense monolayers for a variety of applications and on a variety of surfaces *via* a covalent bond to the surface and among other silanes.[38] However, robust monolayers can only be formed on silanes under very restrict conditions for the hydrolysis of Alkoxy or halogenated silane species, which is dependent on the water content, pH, and temperature. If the hydrolysis is not sufficient (such as when not enough water is present) then a partial monolayer will be formed.[35, 39] On the other hand, if the hydrolysis is extensive (if an excess of water is present) then self–condensation to form Si-O-Si bond will occur and multilayers can be formed on the surface. It is only when the modification conditions can be carefully controlled that robust, well–packed monolayers

can be formed using silanes as illustrated in the figure below. Moreover the storage of silanes has to be anhydrous as they may self-condense with the presence of water in the environment.

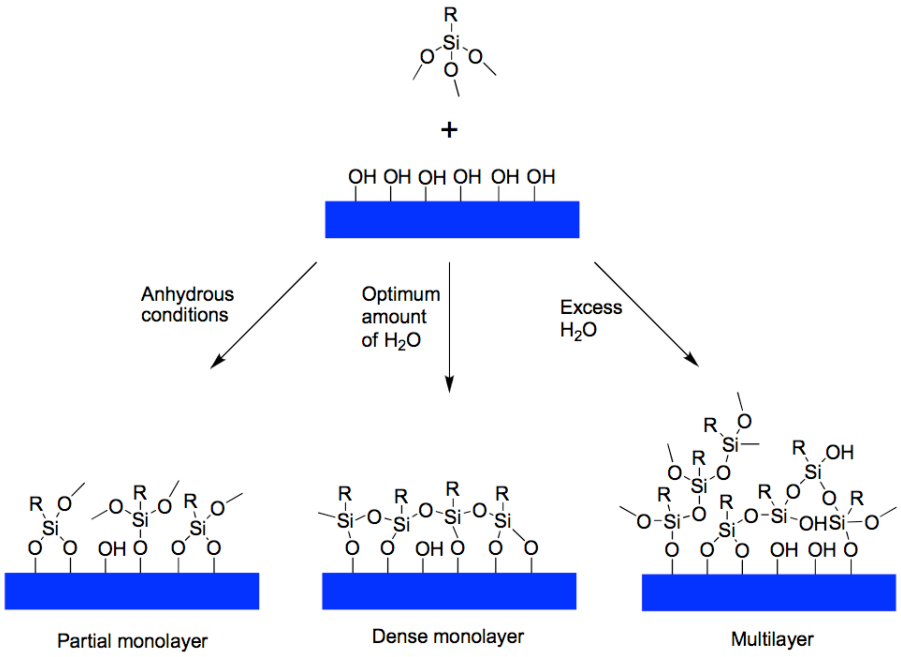

Figure1.2 Illustration showing the impact of water on the formation of monolayers from silanes. Adapted from Mutin *et al.*[39]

Carboxylic acids have been shown to successfully bind to different metal oxides, in a variety of binding modes, including as an uncoordinated anion, a monodentate ligand, a bidentate chelate or a bridging bidentate.[36] Though the high-coverage monolayer can be prepared using carboxylic acids,[42] the binding between surface and molecule was found to be generally very weak so the attached molecules can be easily removed, sometimes even by simple rinsing in solvents.[37] In addition, researchers have shown that the

presence of polar sites on the carboxylic acid molecules can result in competition for surface sites, thus preventing well–organized, high coverage monolayers.[36]

Phosphonic acids were first used as monolayers on metal oxide surfaces in the early nineties[34]. Since then research on phosphonic acids as surface modifiers has been increasing dramatically as advantages (such as hydrolytically robust binding on the surface) with respect to other monolayer-forming species have been revealed in the last decade.

Phosphonic acids, while having similar structure to that of silanes, have very different properties with respect to binding metal oxide surfaces. Phosphonic acids are thought to bind to a metal oxide surface by first coordination of the phosphoryl oxygen to Lewis acidic sites on the surface, followed by condensation of the P–OH groups with surface hydroxyl groups or other surface oxygen species.[35] One of the advantages of utilizing phosphonic acids is that the formation of multilayers as seen for silanes is less likely because the homocondensation of P–OH and P–O bonds does not occur at mild conditions and/or in aqueous conditions.[35] Additionally the extent of hydrolysis does not have an impact on the quality of modification, so less stringent conditions can be applied when using phosphonic acids with respect to silanes. One other advantage of using phosphonic acids is their ambient stability over long periods of time as discussed above.

However one of the drawbacks of phosphonic acid is their limited commercial availability unlike alkoxy and halogenated silanes that are widely available. Also phosphonic acids may form incomplete monolayers if the surface is not heavily hydroxylated,[35] thus the formation of robust, complete monolayers is more dependent on the functional group present on the surface of the oxide such as hydroxyl groups.

Based on relative pros and cons we decided to use phosphonic acids for the surface modification of metal oxides.

1.3.2 Possible Binding Modes of Phosphonic Acid on Metal Oxide Surface

It has been proposed that there are several binding scenarios for phosphonic acid adsorption on transition metal oxide surfaces, which differ in the number of oxygen atoms bound to the surface and the involvement of hydrogen bonding.[40] The type of adsorption mode can change the orientation of the modifier and the net surface dipole at the ITO/modifier interface, which can be important in determining effective surface work function; therefore, it is important to describe the possible binding modes here.

Because there are three oxygen atoms in the phosphonic acid moiety (one phosphoryl oxygen and two hydroxyl oxygen atoms), up to three oxygen atoms can bind to a surface. That is to say the phosphonic acids can bind to a metal oxide surface in either a monodentate, bidentate, or tridentate fashion as illustrated in Figure1.3 below.

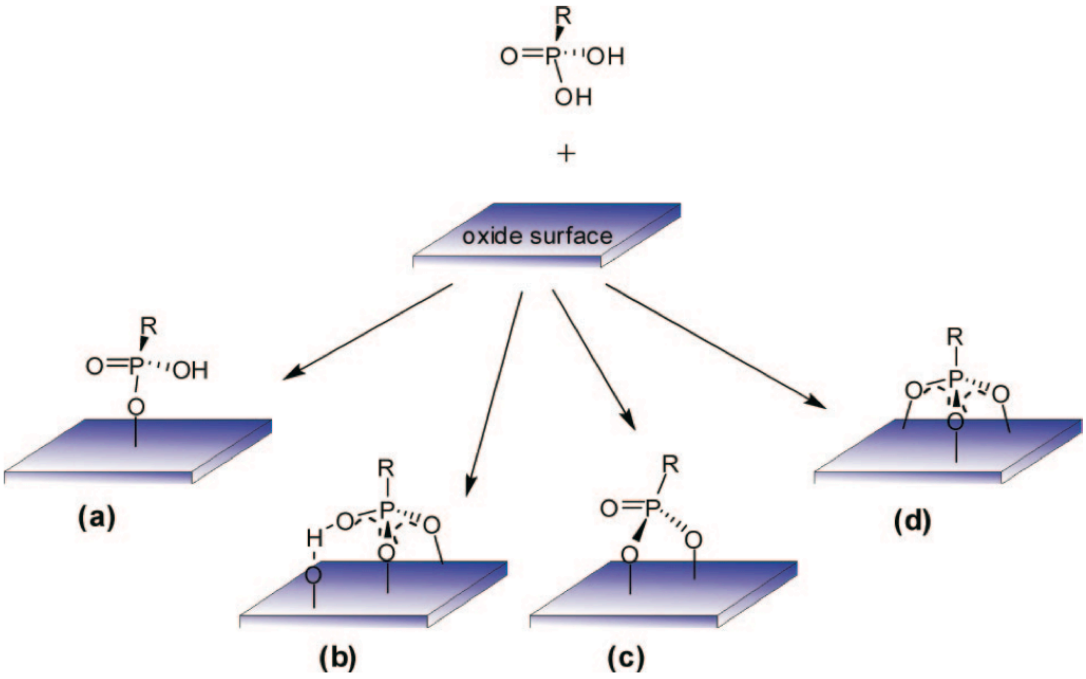

Figure1.3 Possible binding scenarios of phosphonic acid on the metal oxide surface. Adapted from Paramonov *et al*.[40]

Apart from different binding modes, there also can be various degrees of chemisorption and/or hydrogen bonding involved. Additionally, the bonds can be either bridging (where each acid oxygen binds to a different metal atom) or chelating (where two or three of the acid oxygen atoms bind to the same metal atom.[41] All of these variations lead to a large variety of interaction between phosphonic acid and the surface.

1.3.3 Work function study on phosphonic acids

As discussed above, the work function is an important parameter for optimization of the device performance. Base on the purpose of the electrode and magnitude of the energy barrier, the work function can be tuned to increase or decrease to various extent by attaching different organic ligands on the electrode surface such that the negatively charged end of the molecular dipole is directed either away from or towards the surface respectively.[43]

So far, quite a few interesting results have been reported in the literature on work function study using phosphonic acids. One early study was reported by Appleyard *et al.*[44] They reported that the modification of the ITO surface with (trichloromethyl)phosphonic acid, (4–nitrophenyl)phosphonic acid, (2–chloroethyl)phosphonic acid and (aminomethyl)phosphonic acid changed the work function by +0.19 eV, +0.30 eV, -0.14 eV, and +0.18 eV respectively. They then found the modified electrodes reduced turn–on voltages and increased luminance for OLEDs with respect to the devices using unmodified ITO as electrodes.

In 2006, Koh *et al.*[45] published a article presenting the effects of nitrophenylphosphonic acid and cyanophenylphosphonic acid on the work function of ITO. They reported large increases of +0.77eV and +0.60 eV respectively, relative to bare ITO. However, this result is larger than what we found in the experiment. Later this year, Guo *et al.46* reported a decrease in the work function of ITO ($\Delta\Phi$ = -0.28 eV) upon

modification of ITO using quarterthiophene–2–phosphonic acid. In addition, upon doping of the attached monolayer with tetrafluorotetracyanoquinodimethane (F4–TCNQ), they obtained an increase in the work function ($\Delta\Phi$ = +0.35 eV) of the substrate relative to bare ITO. With this monolayer-doped substrate, they reported an increase in both the charge carrier density and the luminance with respect to the unmodified ITO electrodes in a bilayer OLED device.

In 2009, Hotchkiss *et al.*[47] reported the work function changes of ITO upon modification using a series of fluoro-substituted benzylphosphonic acids and reported a comparison of the changes in the work function of the modified ITO as a function of the calculated dipole moment values of the modifiers, in which the slopes of the experimental data is -0.48 eV/Debye. They also reported the comparison of the work function change values obtained from theoretical calculation as a function of the calculated dipole moment values of the modifiers with a slope of -0.39 eV/Debye, which is in good agreement with the experimental values. They successfully used several phosphonic acids to modify the surface of ITO substrates in order to tune the ITO work function absolute value between 4.90 eV and 5.40 eV.

Recently Yu *et al.*[48] demonstrated that the use of mixed phosphonic acid monolayers allows the continuous tuning of the work function of ITO over a wide range. In particular, with mixed monolayers prepared from a mixture of n-butylphosphonic acid and 4,4,4-trifluorobutyl-1-phosphonic acid, the work function of ITO can be tuned over a range from 5.0 to 5.75 eV by varying the mixing ratio of the two adsorbents.

The study in this thesis will focus on the investigation of the relationship of the workfunction changes of the modified surfaces with the varying properties of the functional groups of the phosphonic acids. The phosphonic acids involved in this thesis are listed in Figure 1.4. The electron-withdrawing property of the functional groups increases in the following order: NO_2 > CN > F > H.

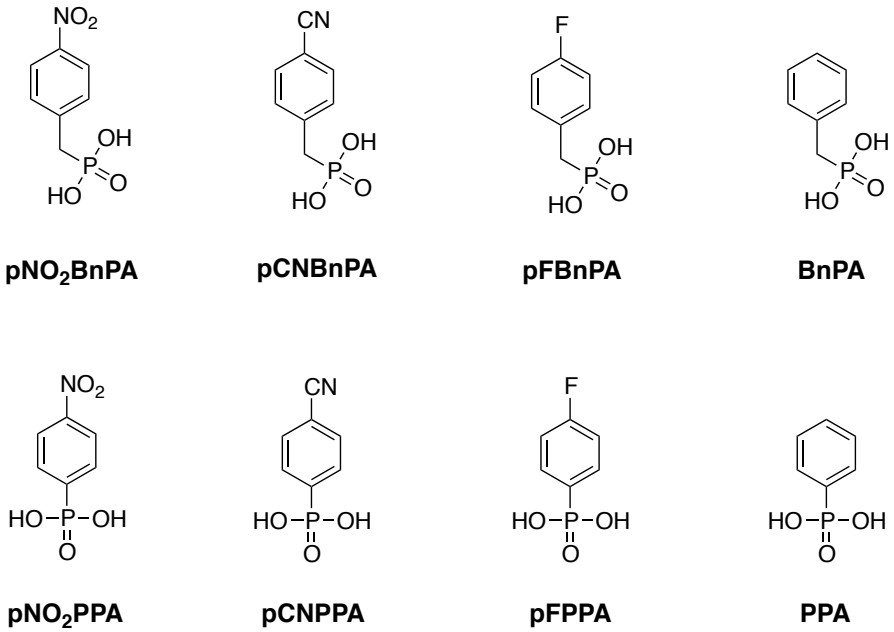

Figure 1.4 Phosphonic acids used in this thesis.

1.4 Organization of the Thesis

This thesis is organized in such a way that readers can first understand the basic concept behind the research work as well as the purpose of this research which are both in the introduction chapter followed by synthesis and characterization of the phosphonic acids. The characterization methods used will be briefly presented followed by the modification work using planar substrates and phosphonic acids. The last section will focus on the discussion based on the characterization of the resulting surfaces, and finally conclusions and appendix.

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CHAPTER 2

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF PHOSPHONATES AND PHOSPHONIC ACIDS

2.1 Synthetic Pathways

There are several methods to synthesize phosphonic acids reported in the literature.[1, 2, 3, 4] The most common way is to first make the dialkylphosphonates, which are key intermediates and then hydrolyze them to give the corresponding phosphonic acids, while there are also alternative ways to make phosphonic acids such as using phosphorus tri– or pentachloride precursors. Here the common way (the first method mentioned above) was followed and the C–P bond was formed by Michaelis–Arbuzov reactions or a catalytic organometallic reaction to make the benzyl and phenyl phosphonates respectively followed by hydrolysis towards the phosphonic acids. All these reactions including conditions and mechanisms[26] will be further discussed in the following sections.

2.1.1 Michaelis – Arbuzov Reaction

Michaelis–Arbuzov reaction (also called the Arbuzov reaction) is the reaction of trialkyl phosphite with an alkyl halide to produce an alkyl phosphonate. The reaction was discovered by August Michaelis in 1898,[5] and widely explored by Aleksandr Arbuzov soon after. This reaction has been widely explored and reviewed afterwards,[6, 7, 8] and is still being explored in more depth.[9] This reaction is extensively used for the preparation of various phosphonates, phosphinates, and phosphine oxides. As illustrated below, the first step of the reaction involves S_N2 nucleophilic attack by the lone pair of phosphorus

on the electrophilic carbon of the alkyl halide to give a phosphonium intermediate (quasiphosphonium ion). The displaced halide anion reacts with the phosphonium intermediate to give the desired phosphonate and another alkyl halide under S_N2 mechanism in the second step. It has been shown that if chiral phosphonium intermediates are produced, the halide substitution proceeds with inversion of configuration as expected by a S_N2 reaction[6].

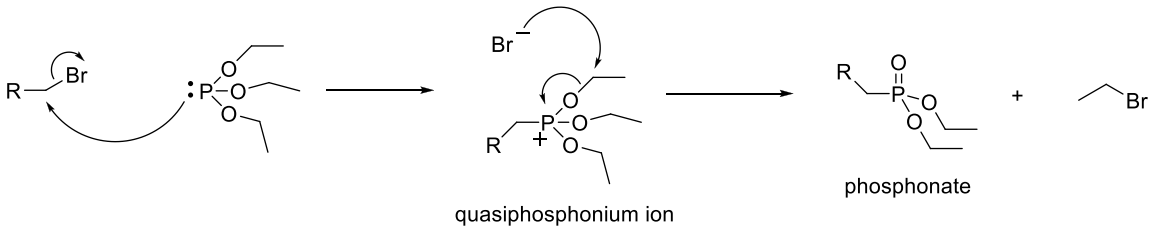


Figure 2.1 Mechanism of the Michaelis – Arbuzov reaction.

Generally the reactivity of the organic halide is in the following order (from most reactive to least reactive): RCOX > RCH_2X > RR'CHX >> RR'R"CX and RI > RBr > RCl.

Also the Arbuzov reactions can take place under microwave irradiation.[7, 10] It has been shown to largely reduce reaction time (from several hours to several minutes) with high yield.[11]

2.1.2 Organometallic Reactions

It has been reported the aryl C–P bond formation can take place using transition metal catalysts such as nickel,[12] copper,[13, 14] and palladium.[15] Different transition metals will lead to different reaction mechanisms. Here the palladium is used to do the reactions.

The first use of palladium salts in the organometallic reaction for the aryl C–P bond formation was reported by Hirao *et al.*[16, 17] As illustrated below in the catalytic cycle palladium species and aryl halide undergo an oxidative addition to form the palladium – aryl complex. Then the added dialkylphosphite and the complex will undergo an exchange reaction to give the arylphosphonate. Finally an amine is used to react with the arylphosphonate (reductive elimination) to regenerate Pd(0) species.

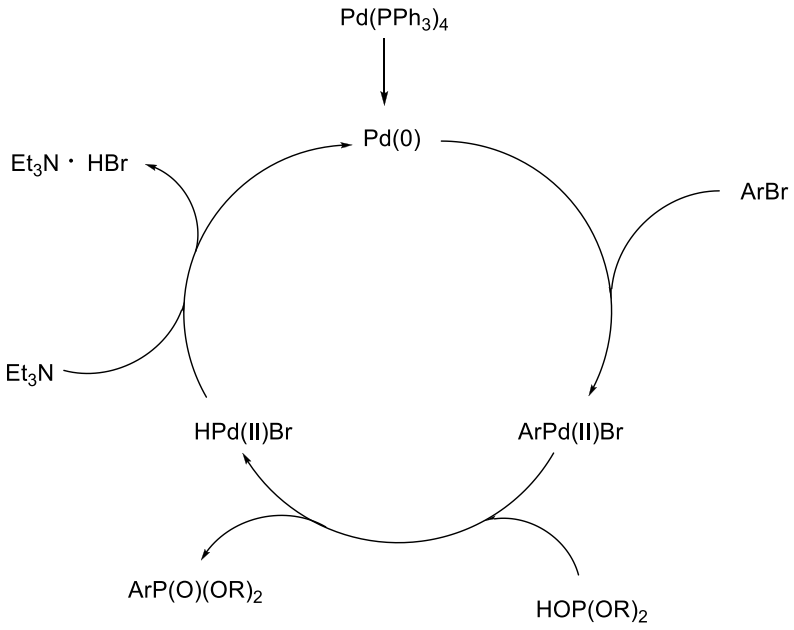


Figure 2.2 Mechanism of the catalytic cycle forming aryl C-P bonds by using palladium salt.

Here the organic reagents are picked according to a paper published in 2005[18] in which the optimized condition (shown in Figure 2.3) is to use polar solvents such as ethanol to reflux. Palladium acetate acts as the best yielding palladium source, and bulky tertiary amines (dicyclohexylmethylamine) with low nucleophilicity can help increasing the reaction's yield.

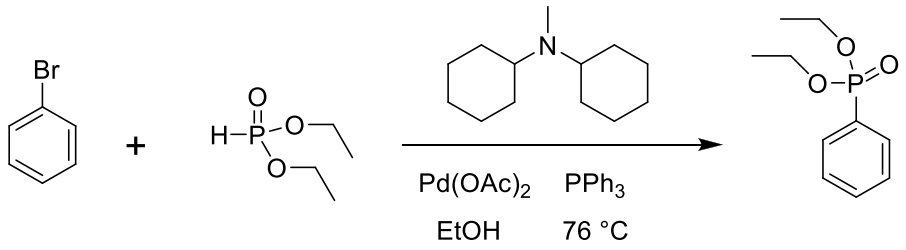


Figure 2.3 Optimized reaction condition for palladium catalyzed aryl C–P bond formation.

2.1.3 Hydrolysis of Phosphonates to Form Phosphonic Acids

There are several ways to prepare phosphonic acids, one of which is to hydrolyze the phosphonates. This is a very common and simple synthetic pathway especially when the phosphonates have been made. The purification step (recrystallization) of this reaction is relatively simple and effective.

There are two widely employed methods for hydrolysis. One is to use concentrated hydrochloric acid.[19] This method usually involves refluxing the concentrated hydrochloric acid with phosphonate for several hours. Upon cooling the reaction, the phosphonic acid solid will precipitate at the bottom of the reaction vessel. However, since the concentrated hydrochloric acid will create strongly acidic conditions for the reaction, this method cannot be used for compounds that contain acid sensitive functional groups.

If the above conditions are too harsh, an alternative hydrolysis method[20] that can be applied involves bromotrimethylsilane (TMSBr) to react repeatedly with dissolved phosphonate to form bis(trimethylsilyl)phosphonate which can then be hydrolyzed to the respective acids upon contact with water and a low boiling point alcohol at room temperature.

The mechanism of this two-step reaction is analogous to the Arbuzov reaction, where the lone pair on the phosphoryl oxygen attacks the partially positive silicon atom of TMSBr. The displaced halide ion then attacks one of the alkoxy groups of the phosphonate, and the alkyl trimethylsilyl phosphonate is formed. Repetition of this cycle results in the substitution of the ethyl group with trimethylsilyl group to give the bis(trimethylsilyl)phosphonate, which will finally form the phosphonic acid in the proton rich condition as shown in Figure 2.4.

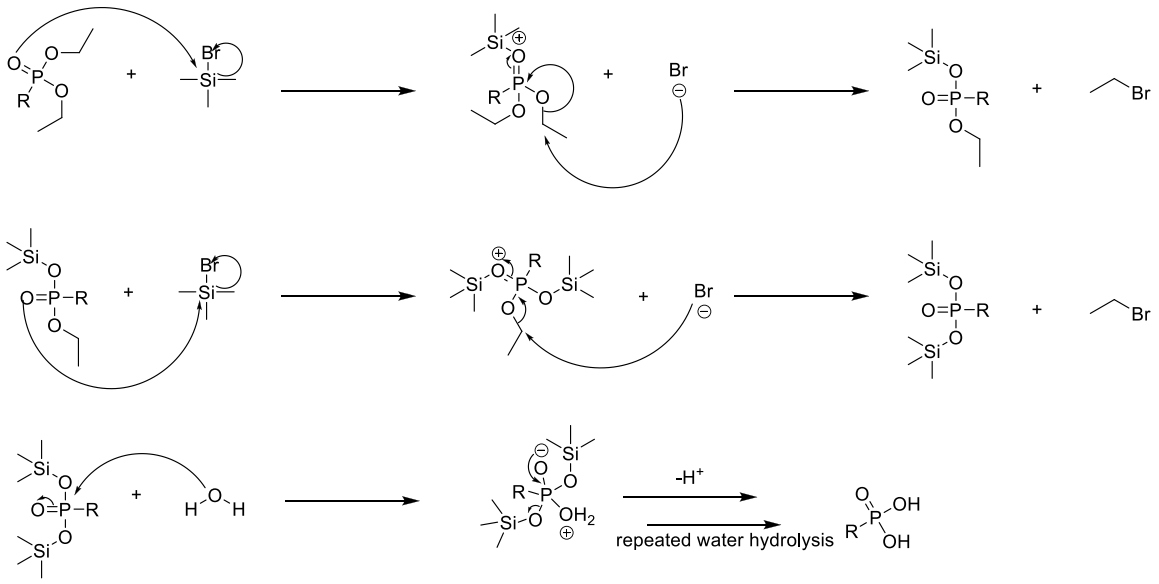


Figure 2.4 Mechanism of hydrolysis of a dialkylphosphonate with bromotrimethylsilane.

2.2 Notes on Synthesis Procedures

The reactions to synthesize phosphonates usually lead to impurities in the reaction mixture when completed. They can be purified using either vacuum or column chromatography (stationary phase: silica gel). The mobile phase is oftentimes a combination of ethyl acetate and hexanes. The phosphonate moiety is stable on silica gel,

usually the compound can be visualized with a standard handheld UV lamp. Sometimes staining agents such as iodine have to be employed to view spots more clearly on silica thin layer chromatography (TLC) plates. Phosphonates are usually in the liquid state at room temperature and are soluble in many solvents, such as ethyl acetate, ether, dichloromethane, chloroform, and acetone.

The reactions to synthesize phosphonic acids are usually simple and easy to conduct unless there are functional groups present on the molecule that are sensitive to acidic conditions. The acidity of the phosphonic acids and their high degree of polarity make them immobile on silica gel. Recrystallization is often used to purify phosphonic acids. However, if recrystallization is not successful, rehydrolysis of the reaction mixture to convert any remaining phosphonate to the phosphonic acid can sometimes be helpful in the purification step. Phosphonic acids are usually solids at room temperature and soluble in polar, protic solvents such as DMSO and ethanol, though usually not water unless the R–group on the phosphonic acid is also polar and/or protic. The phoshonates and phosphonic acids that have been synthesized are stable in the air.

It is also important to note that other functional groups present on the molecule have to be tolerant to the reaction conditions and compatible with the phosphonic acid itself, so any groups sensitive to acid might not survive on the same molecule. There was an issue when attempting to synthesize (4-formylphenyl)phosphonate and (4-formylphenyl)phosphonic acid in our lab. The purification step in making the (4-formylphenyl)phosphonate was more complicated than the phosphonates with other functional groups in the *para* position. Several side products moved closely with the desired phosphonate on the silica gel, so it took several times to run the columns until the desired phosphonate was pure. The hydrolysis reaction turned out to be more problematic than the previous reaction using the pure synthesized (4-formylphenyl)phosphonate as the starting reactant. The pure desired product could not be obtained using any of the routine methods without protecting the aldehyde group on the aromatic ring at the first place.

2.3 Experimental

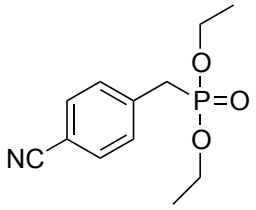
^{1}H spectra were obtained on a Varian Mercury 300 MHz or 400 MHz spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as the reference.

^{13}C NMR spectra were obtained with proton decoupling on a Varian Mercury 300 MHz or 400 MHz spectrometer.

^{31}P NMR spectra were obtained with proton decoupling on a Varian Mercury 400 MHz spectrometer using H_3PO_4 in a capillary tube as an external reference.

High-Resolution Mass spectra were obtained by GT Mass Spec Lab using either electron impact (EI) of fast atom bombardment (FAB) mode.

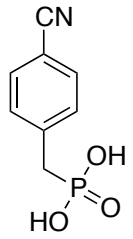
Elemental analyses were carried out by Atlantic Microlabs using a LECO 932 CHNS elemental analyzer.



Diethyl 4-cyanobenzylphosphonate

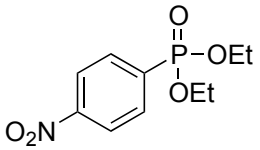
4-(Bromomethyl)benzonitrile (9.0 g, 45.9 mmol) and a magnetic stir bar were put in a 100 ml round bottom flask fitted with a reflux condenser, and the system was purged with nitrogen for about half an hour before adding triethyl phosphite (23.6 ml, 138 mmol) and heating. The mixture was refluxed overnight at 150 °C. The excess triethyl phosphite

was removed by vacuum distillation to afford the product as yellow oil (GHF-I-028A; 9.43 g, 81.3%). The ^{1}H NMR spectrum is consistent with the desired product. [21]



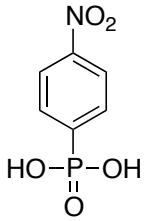
4-Cyanobenzylphosphonic acid

Diethyl 4-cyanophenylphosphonate (5.0 g, 19.7 mmol) was added in a round bottom flask with a stir bar inside and dichloromethane (63.3 ml, from the solvent purification system) was added in order to completely dissolve the phosphonate. The mixture was allowed to stir for approximately 15 minutes. TMSBr (7.82 ml, 59.2 mmol) was then added and the system was sealed with a greased stopper. The mixture was allowed to react at room temperature overnight. Volatiles were removed under reduced pressure and to the resulting oil was added methanol and water. The vessel was sealed with a rubber septum and a needle inserted for the escape of any excess TMSBr. The mixture was allowed to stir at room temperature overnight. The resulting white solid (GHF-I-038A; 3.39 g, 87.2%) was recrystallized from acetonitrile. The ^{1}H NMR spectrum is consistent with the desired product. [22]



Diethyl 4-nitrophenylphosphonate

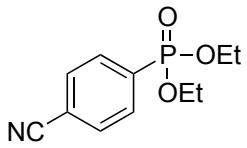
1-Bromo-4-nitrobenzene (10.0 g, 49.5 mmol), palladium(II) acetate (222 mg, 1.0 mmol)and triphenylphosphine (780 mg, 2.97 mmol) were added into a 500 ml round bottom flask with a condenser and magnetic stir bar. The vessel was purged with nitrogen for 15minutes. Then ethanol (~200 ml) was added along with diethylphosphite (7.7 ml) and dicyclohexylmethylamine (21.0 ml) via syringe. The mixture was refluxed for 16 hours and then diluted with ethyl acetate (~300 ml). Washing was done using 1 M HCl, saturated $NaHCO_3$ and brine solution. The organic layer was then dried with $MgSO_4$. The organic solvent was removed under reduced pressure to give dark yellow oil followed by purification using column chromatography to yield dark orange oil (GHF-I-026A; 2.27 g, 17.8%). The ^1H NMR spectrum is consistent with the desired product. [23]



4-Nitrophenylphosphonic acid

Diethyl 4-nitrophenylphosphonate (2.28 g, 8.80 mmol) was added in a round bottom flask with a stir bar inside and dichloromethane (28.2 ml, from the solvent

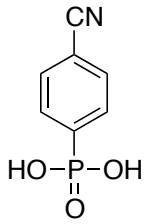
purification system) was added in order to completely dissolve the phosphonate. The mixture was allowed to stir for approximately 15 minutes. TMSBr (3.48 ml, 26.4 mmol) was then added and the system was sealed with a greased stopper. The mixture was allowed to react at room temperature overnight. Volatiles were removed under reduced pressure and to the resulting oil was added methanol and water. The vessel was sealed with a rubber septum and a needle inserted for the escape of any excess TMSBr. The mixture was allowed to stir at room temperature overnight. The resulting gray solid (GHF-I-032E; 900 mg, 50.5%) was recrystallized from acetonitrile. The ^{1}H NMR spectrum is consistent with the desired product. [24]



Diethyl 4-cyanophenylphosphonate

1-Bromo-4-cyanobenzene (15.0 g, 82.4 mmol), palladium(II) acetate (370 mg, 1.65 mmol)and triphenylphosphine (1.3 g, 4.94 mmol) were added into a 500 ml round bottom flask with a condenser and magnetic stir bar. The vessel was purged with nitrogen for 15 minutes. Then ethanol (336 ml) was added along with diethylphosphite (12.7 ml) and dicyclohexylmethylamine (35.0 ml) via syringe. The mixture was refluxed for 16 hours and then diluted with ethyl acetate (~300 ml). Washing was done using 1 M HCl, saturated $NaHCO_3$ and brine solution. The organic layer was then dried with $MgSO_4$. The organic solvent was removed under reduced pressure to give dark yellow oil followed by

purification using column chromatography to yield yellow oil (GHF-I-030C; 5.43 g, 27.6%). The ^{1}H NMR spectrum is consistent with the desired product.[25]



4-Cyanophenylphosphonic acid

Diethyl 4-cyanophenylphosphonate (5.4 g, 22.7 mmol) was added in a round bottom flask with a stir bar inside and dichloromethane (72.8 ml, from the solvent purification system) was added in order to completely dissolve the phosphonate. The mixture was allowed to stir for approximately 15 minutes. TMSBr (9.0 ml, 68.1 mmol) was then added and the system was sealed with a greased stopper. The mixture was allowed to react at room temperature overnight. Volatiles were removed under reduced pressure and to the resulting oil was added methanol and water. The vessel was sealed with a rubber septum and a needle inserted for the escape of any excess TMSBr. The mixture was allowed to stir at room temperature overnight. The resulting white solid (GHF-I-040A; 2.35 g, 56.6%) was recrystallized from acetonitrile. ^{1}H NMR (300.22 MHz, DMSO) δ 7.76–7.83 (m, 2H), 7.89–7.93 (m, 2H). ^{13}C{^{1}H} NMR (100.58 MHz, DMSO) δ 139.93 (d, J = 237.4 Hz), 132.47 (d, J = 18.1 Hz), 131.60 (d, J = 13.1 Hz), 118.83 (d, J = 2.0 Hz), 113.77 (d, J = 2.0 Hz). ^{31}P{^{1}H} NMR (161.97 MHz, DMSO): δ 10.38. Analysis calculated (found) %: C 45.92 (45.94), H 3.30 (3.25). Exact mass calculated (found) for $[M]^{+}$ (EI, m/z): 183.0088 (183.0077).

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CHAPTER 3

MODIFICATION OF PLANAR ITO SURFACES AND MEASUREMENTS OF THE MODIFIED SURFACES

In this chapter efforts to modify planar ITO surfaces using phosphonic acids will be discussed. A brief overview of the substrates that have been modified by phosphonic acids will be given and emphasis will be given on indium tin oxide (ITO). The modification methods will then be described. The surface characterization results will be presented and analyzed following the introduction of each characterization method.

3.1 Background of Planar Substrates that Have Been Modified with Phosphonic Acids

In the literature, a number of planar substrates have been reported to be modifiable with phosphonic acids. Metal oxide includes indium tin oxide (ITO),[1, 2] copper oxide,[3] aluminum oxide,[4, 5] tantalum oxide,[6, 7] hafnium oxide,[8] nickel oxide,[9] iron oxide,[10] chromium oxide,[11] niobium oxide,[12] zirconium oxide,[13] native oxide on titanium,[14, 15] and various forms of silica.[4, 16, 17 18] Some common metal alloys such as brass[3] and steel,[11] can also be modified. Quite a few papers have been published on modification of ITO, aluminum oxide, copper (II) oxide and various forms of silica as substrates to modify with phosphonic acids in particular. Indium tin oxide (ITO) is used in this thesis to study the role that phosphonic acids can play to modify work function of metal oxides, due to its importance as a hole-injecting and collecting electrode in organic electronics.

Indium tin oxide (ITO) is currently the most widely used transparent electrode in opto-electronic thin-film devices such as organic light-emitting diodes, liquid crystal

displays, and solar cells. However there are several drawbacks for ITO, such as poor compatibility and substantial hole-injection barrier at the organic/inorganic interface,[19] which will lower the device efficiency. Considerable effort has thus been placed on improving the properties of these interfaces through chemical modification of the ITO surface via self-assembling organic small-molecule monolayers on the surface as well as through theoretical calculation.[1, 20, 21, 22]

3.2 Methods of Surface Modification

Planar metal oxides can be modified in a number ways with phosphonic acids. Thus far the methods include tethering by aggregation and growth (T–BAG),[17] dip–coating,[23] spincoating,[4, 24] microcontact printing.[18, 25] and spray–coating,[26]

In 2003 Hanson *et al*.[17] reported the T–BAG (tethering by aggregation and growth) procedure, which has been widely used and optimized since its first development. This procedure involves holding the substrate vertically in a solution of phosphonic acid and letting the solvent evaporate over time until the solvent level falls below the substrate area (as shown in Figure 3.1). The authors reported that when the solvent evaporates, the phosphonic acid molecules are transferred to the surface in an organized fashion as a result of their amphiphilic nature at the solvent/air interface.[17]

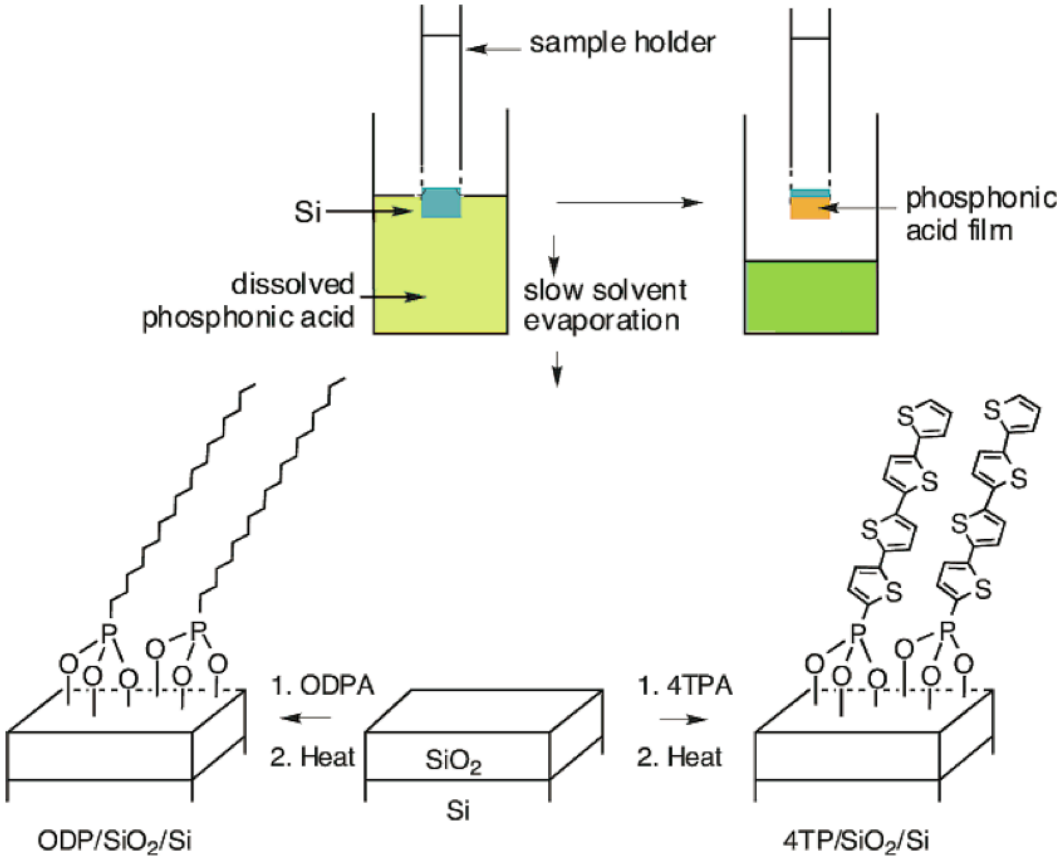

Figure 3.1 The T-BAG setup and chemical reactions; colors shown for an example (4TPA). Adapted from Hanson *et al*.[17]

After the solvent level reaches below the substrate edge, the substrate can be rinsed and then placed in an oven (~ 140 °C) for a period of time (typically between hours and days). This is to complete the heterocondensation reaction of the phosphonic acid onto the surface. After heating, the substrate is rinsed in a weak base to remove any unbound or weakly bound phosphonic acid molecules.

Regarding what solvents can be used to successfully grow monolayers of phosphonic acids on metal oxides, discussion is in progress in the literature. Polar solvents such as ethanol, 2–propanol and tetrahydrofuran have been found to be the

suitable solvents and are commonly used. On the other hand Nie *et al*.[4] have reported on the use of relatively nonpolar solvents, such as toluene and trichloroethylene, which gave better monolayer coverage on mica, Si/SiO_x, and Al/AlO_x with respect to polar solvents. Water has also been used in certain systems as well.[11]

The modification method used in the experiments described herein is a modified T–BAG method, in which the cleaned substrates are fully immersed in the solution horizontally or at an angle, by leaning them on the inside wall of solution container. The same rinsing steps as for the T–BAG method were used; the details are reported in the experimental section of this chapter.

3.2.1 Modification of ITO With Phosphonic Acids

It has been demonstrated that metal oxides can play important roles in a variety of technologies. Transparent metal oxides, such as ITO, can be used as electrodes in organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs). There are a number of papers published on the surface modification of ITO with phosphonic acids in order to improve various properties, such as increasing hole injection efficiency in OLEDs.[27, 28, 29] ITO can be modified in various ways in order to change the surface properties using special techniques or materials. One of them is to modify the surface properties by depositing a monolayer of organic compounds.[28, 30] In the literature, phosphonic acids, silanes and carboxylic acids have all been popular choices as surface modifiers for ITO surfaces.[1, 27, 17, 31, 32]

This chapter describes our work on the modification of ITO with phosphonic acids to tune the work function of the ITO surface, which was achieved via design and synthesis of phosphonic acids that have dipoles of various magnitudes and depositing them onto the surface of ITO. The work functions of the modified surfaces were

measured by Yinhua Zhou (Electrical and Computer Engineering, Georgia Tech) using the Kelvin Probe. The XPS measurement was done by myself.

3.3 Photoelectron Spectroscopy

This section provides a brief description of the experimental technique used for the research presented in this thesis. Photoelectron Spectroscopy (PES) is based on the photoelectric effect discovered by Hertz in 1887. The basic idea of the photoelectric effect is that electrons escape from a material after the absorption of energy from electromagnetic radiation. Einstein first explained the principle theoretically in 1905 by the introduction of the concept of photons carrying a quantized energy hν. This theory gives rise to several types of photoelectron spectroscopy, such as X–ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS), Auger Electron Spectroscopy (AES) and Electron Spectroscopy for Chemical Analysis (ESCA).[33] By measuring the kinetic energy of the ejected electrons, insights about the inner electronic structure of the material can be gained. As the experimental possibilities have developed, increasing accuracy can be achieved, yielding more detailed information.[34, 35] Nowadays PES has developed into a widely used technique used for all kinds of surface analysis.

3.3.1 X–Ray Photoelectron Spectroscopy

For the investigation discussed in this thesis, X-ray Photoelectron Spectroscopy (XPS) was used as the characterization tool for surface properties. XPS is a sensitive quantitative spectroscopic technique that can be used to identify the elements that present in the top layers of a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously collecting the escaped electrons and measuring the kinetic energy and number of electrons that escaped from the top 10 nm or less of the

material being analyzed. In X-ray Photoelectron Spectroscopy (XPS) the most commonly used beam sources are Mg(K_α) or Al(K_α) radiation corresponding to photon energies of 1253.7 eV and 1486.6 eV respectively. With XPS, the core levels of the elements within the material are investigated and since each element has a unique binding energy, information regarding elemental composition, empirical formula, chemical state and electronic state of the sample can be observed. Since changes in the chemical environment of an element affect core- and valence-level binding energies, processes such as doping, oxidation and molecular adsorption can be changed and are detected as core level shifts.

3.4 Results and Discussion

This section mainly shows the results of work function changes of modified ITO surfaces as well as the results from XPS measurements of the modified ITO surfaces.

3.4.1 Work Function Changes of ITO Substrates Using Phosphonic Acids

Our efforts on work function tuning focused on modifying ITO using eight different phosphonic acids (listed in Figure 3.2). The different phosphonic acids were chosen such that the head group substituents exhibit a variety of electron-withdrawing ability. In terms of electron-withdrawing property, they follow the increasing order of NO_2 > CN > F > H. Two families of different derivatives have been studied: benzyl phosphonic acids and phenyl phosphonic acids as shown below.

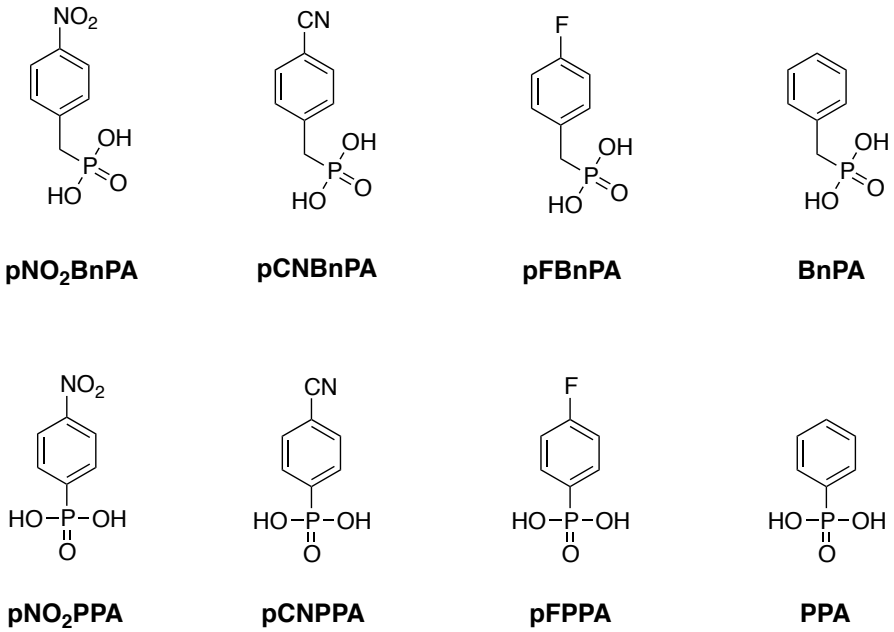

Figure 3.2 Chemical structures of phosphonic acids used in the work function study: 4-nitrobenzylphosphonic acid (pNO_2BnPA) (AJG-III-005B), 4-cyanobenzylphosphonic acid (pCNBnPA) (GHF-I-038A), 4-fluorobenzylphosphonic acid (pFBnPA) (AJG-III-11A), benzylphosphonic acid (BnPA) (AJG-III-073D), 4-nitrophenylphosphonic acid (pNO_2PPA) (GHF-I-032E), 4-cyanophenylphosphonic acid (pCNPPA) (GHF-I-040A), 4-fluorophenylphosphonic acid (pFPPA) (PJH-III-054C), phenylphosphonic acid (PPA) (Commercially available).

The modified T–BAG method was used to grow these phosphonic acids on ITO surfaces. Work function values were obtained using Kelvin Probe. The ITO substrates were cleaned in two ways: one is detergent/solvent cleaning (DSC) and the other is detergent/solvent cleaning plus oxygen plasma–etching (DSC/OP). Work function change values ($\Delta\Phi$) of PA modified ITO surfaces was obtained by comparing the measured work function of the PA modified surfaces to the cleaned ITO surface that was soaked overnight in absolute ethanol. Samples are compared separately in terms of DSC

and DSC/OP cleaning protocol and in terms of benzyl and phenyl phosphonic acid to find the differences. The values are shown in Table 3.1 below.

Table 3.1 Work function changes (ΔΦ) of ITO surfaces modified by different phosphonic acids, obtained from Kelvin Probe measurements. Part a shows data for benzylphosphonic acids and phenylphosphonic acids using the DSC cleaning procedure, part b shows data using the DSC/OP procedure)

a) DSC

Modifier (BnPA)	pNO_2BnPA	pCNBnPA	pFBnPA	BnPA
ΔΦ (eV)	0.396 (±0.014)	0.271 (±0.019)	0.115 (±0.011)	-0.030 (±0.008)
Modifier (PPA)	pNO_2PPA	pCNPPA	pFPPA	PPA
ΔΦ (eV)	0.137 (±0.022)	0.195 (±0.010)	0.082 (±0.015)	0.011 (±0.002)

b) DSC/OP

Modifier (BnPA)	pNO_2BnPA	pCNBnPA	pFBnPA	BnPA
ΔΦ (eV)	0.530 (±0.024)	0.517 (±0.017)	0.185 (±0.021)	-0.046 (±0.007)
Modifier (PPA)	pNO_2PPA	pCNPPA	pFPPA	PPA
ΔΦ (eV)	0. 287 (±0.013)	0.305 (±0.023)	0.160 (±0.028)	0.020 (±0.004)

From the work function changes, we can obtain the following information: First, the DSC/OP samples have larger work function changes than the corresponding DSC samples. Second, the work function changes of ITO surfaces modified by benzylphosphonic acids follow the same order (pNO_2BnPA > pCNBnPA > pFBnPA > BnPA) for both DSC and DSC/OP cleaning. Third, the work function is increased if we introduce an electron-withdrawing group at the *para* position on the aromatic ring of phosphonic acids thus creating a dipole pointing outwards the surface. The reasoning and analysis will be discussed more in detail in Chapter 4. Fourth, the absolute value of $\Delta\Phi$ is larger for benzylphosphonic acids than phenylphosphonic acids, which might be due to the fact that benzylphosphonic acids have a flexible CH_2 group, and could result in larger dipole moments perpendicular to the surface thus increasing the work function further assuming the same coverage density of PA molecules on the surface.

3.4.2 XPS Characterization

XPS spectra were obtained to confirm that the different phosphonic acids are bounded onto the surface, survey scans and high-resolution scans for the largest peaks for each element were recorded. By comparing the P/In ratios for ITO surfaces modified by different phosphonic acids listed in Table 3.2, we can obtain the information related to the relative surface coverage of the modifiers on ITO surfaces.

Table 3.2 P/In ratios of ITO surfaces modified by different phosphonic acids. Obtained from XPS. (Part a shows data for benzylphosphonic acids and phenylphosphonic acids using the DSC cleaning procedure, part b shows data using the DSC/OP cleaning procedure)

a) DSC

Modifier (BnPA)	pNO_2BnPA	pCNBnPA	pFBnPA	BnPA
P/In ratio	0.044 (±0.018)	0.053 (±0.012)	0.105 (±0.006)	0.123 (±0.003)
N/In or F/In ratio	0.042 (±0.002)	0.061 (±0.007)	0.108 (±0.023)	—
Modifier (PPA)	pNO_2PPA	pCNPPA	pFPPA	PPA
P/In ratio	0.050 (±0.016)	0.058 (±0.010)	0.160 (±0.004)	0.221 (±0.002)
N/In or F/In ratio	0.058 (±0.007)	0.069 (±0.006)	0.149 (±0.011)	—

b) DSC/OP

Modifier (BnPA)	pNO_2BnPA	pCNBnPA	pFBnPA	BnPA
P/In ratio	0.117 (±0.012)	0.133 (±0.013)	0.149 (±0.024)	0.162 (±0.015)
N/In or F/In ratio	0.101 (±0.008)	0.126 (±0.011)	0.164 (±0.016)	—

Table 3.2 continued

Modifier (PPA)	pNO_2PPA	pCNPPA	pFPPA	PPA
P/In ratio	0.129 (±0.022)	0.144 (±0.011)	0.260 (±0.020)	0.271 (±0.013)
N/In or F/In ratio	0.105 (±0.007)	0.122 (±0.010)	0.257 (±0.017)	—

As shown in Table 3.2, in contrast to the bare ITO, all of the P/In ratios are positive showing the presence of P atom on the surface, which is the direct evidence that the ITO surfaces have been successfully modified by the phosphonic acids.

Each phosphonic acid molecule has one phosphorus atom; the more phosphorus atom per surface unit cell the larger coverage density the sample has. So by comparing the P/In ratios we can obtain the information about the relative coverage of phosphonic acids on the ITO surfaces. In addition, each molecule also has one N or F atom if it has one. Thus the N/In or F/In ratios should follow the same trends as the corresponding P/In ratios.

Data in Table 3.2 a) also indicates that the relative coverage is in the following order: pNO_2BnPA < pCNBnPA < pFBnPA < BnPA, and it follows the same trend for PPAs (pNO_2PPA < pCNPPA < pFPPA < PPA). If we use the DSC/OP cleaning procedure, the same trend follows as shown in Table 3.2 b).

In the comparison on coverage between benzylphosphonic acids and phenylphosphonic acids, pNO_2BnPA < pNO_2PPA; pCNBnPA < pCNPPA; pFBnPA < pFPPA; BnPA < PPA. The larger coverage density of phenylphosphonic acids could be caused by the absence of the flexible CH_2 linking group, which allows for more molecules to be attached to the surface per unit square area. When comparing between

the two cleaning procedures, samples that have been cleaned by DSC/OP have larger coverage than DSC procedure for all phosphonic acids, which might because the oxygen plasma cleaning can remove surface contaminants more effectively than the DSC cleaning thus working favorably for deposition of phosphonic acids on the ITO surfaces. Or it could because the oxygen plasma cleaning can make the surface more reactive.

3.5 Experimental

Procedures for modification of ITO with phosphonic acids:

I) Cleaning:

All ITO:Glass substrates were cleaned by DSC or DSC/OP procedure which includes the following steps:

1) Scrubing/washing ITO substrates for ~5-10 minutes with a lens cloth and Triton-X 100 surfactant & using running water and plenty of surfactant.

2) Sonicating the substrates in a Triton-X 100 solution in deionized water for 10 minutes & then washing with deionized water.

3) Sonicating the substrates in deionized water for 10 minutes & washing with deionized water.

4) Sonicating the substrates in ethanol for 10 minutes & washing with ethanol.

5) For samples that need plasma cleaning, cleaning the substrates with oxygen plasma etcher (Harrick, model PDC–32G operated at 60 W) for 5 minutes (face up).

II) Modification (modified T–BAG procedure):

Following the cleaning steps, immediately submersed the substrate into a 10 mM solution of the phosphonic acid of choice (in ethanol). Placed the substrate on a little vial

cap (optional), facing up, allowing the substrate to react with the phosphonic acid in solution overnight. (See Figure 3.4 below)

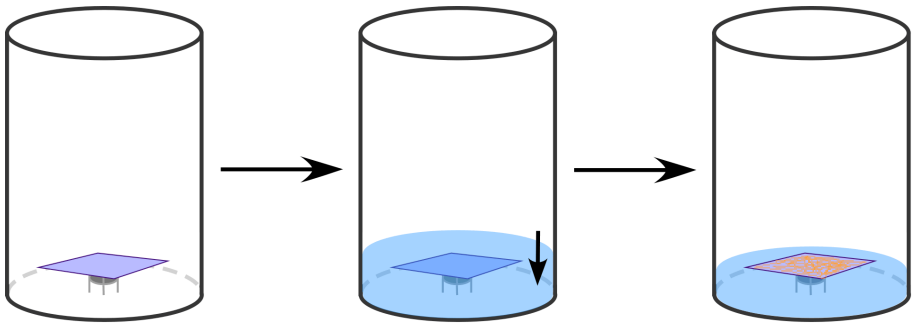

Figure 3.3 The ITO substrate is placed on a vial cap (optional) and then the container filled with the solution of phosphonic acid. Over time the phosphonic acid molecules will be adsorbed onto the ITO surface.

III) Post-modification washing and drying:

Following the modification, the ITO substrates were removed from the solution then sonicated in a 5% triethylamine/ethanol solution, followed by rinsing with absolute ethanol for 10 minutes to remove any multilayer materials that are weakly bound to the monolayer and then use N_2 gun to blow it until completely dry. Finally the modified substrates were stored in plastic sample holders and got measurements.

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CHAPTER 4

THESIS CONCLUSIONS

This thesis presents our work on surface modification of ITO surfaces to understand the effect of different functional groups of phosphonic acids have on work function of ITO surfaces after attachment of those said phosphonic acids.

To investigate the properties of the modified ITO surfaces, work was done involving design and synthesis of the surface modifiers (phosphonic acids), surface modification reactions and characterization the modified surfaces. The following paragraphs provide a summary of the presented work as well as the conclusion drawn from the experimental results.

The synthesis of several phosphonic acids has been reported in Chapter 2 of this thesis. They have similar structures with different head groups with varying properties. We chose these molecules since we are interested in investigating the relationship between work function changes of the modified surfaces with head group properties of the phosphonic acids. The desired phosphonic acids have been synthesized and expertise was gained in what procedures usually work for synthesizing the precursor phosphonates and the phosphonic acids.

The surface modification reaction was done using the modified T-BAG method described in Chapter 3. Immediately following the surface modification, characterization of the fresh ITO surfaces was conducted to eliminate the errors correlated to contamination of the surfaces by the atmosphere.

Our work focused on the work function changes of the different modified surfaces in order to find the evolution of work function changes with the different phosphonic acid molecules as surface modifiers. Apart from the theories that have been demonstrated in Chapter 1, experimental data is also needed to achieve the goal of the research. Work

functions of ITO samples were measured by Kelvin Probe; the elemental composition of the surfaces was characterized by XPS, from which we can also obtain the information about the relative coverage of phosphonic acids on the surfaces.

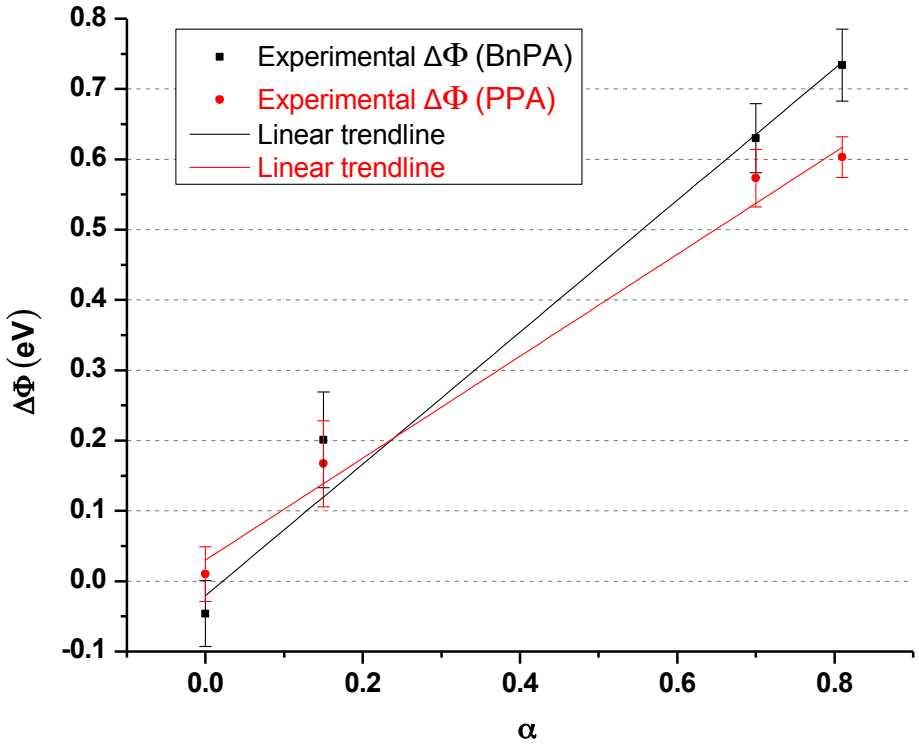
As shown in Chapter 3, DSC/OP method works better to clean the surface of ITO than the DSC method, and can lead to a better coverage density of the phosphonic acids on the ITO and larger work function changes. So to compare the relationships between the work function changes and different functional groups of the phosphonic acids, only the experimental data obtained for the DSC/OP cleaned samples are considered here.

The coverage density of phosphonic acids on the ITO surfaces is an important factor determining the work function changes of the modified surfaces. According to the theory mentioned in Chapter 1, the larger the coverage density, the more PA molecules would be attached to the unit surface area on the ITO, the larger the work function change of ITO would be achieved. However, the XPS data presented in Chapter 3 indicated that the coverage are different for different surface modifiers. Thus to compare the work function changes, the coverage densities of the ITO surfaces by different phosphonic acids needs to be normalized to the same level, i.e. we need to normalize the work function changes of the ITO surfaces for a hypothesis case where the PA molecules cover the ITO surfaces to the same extent.

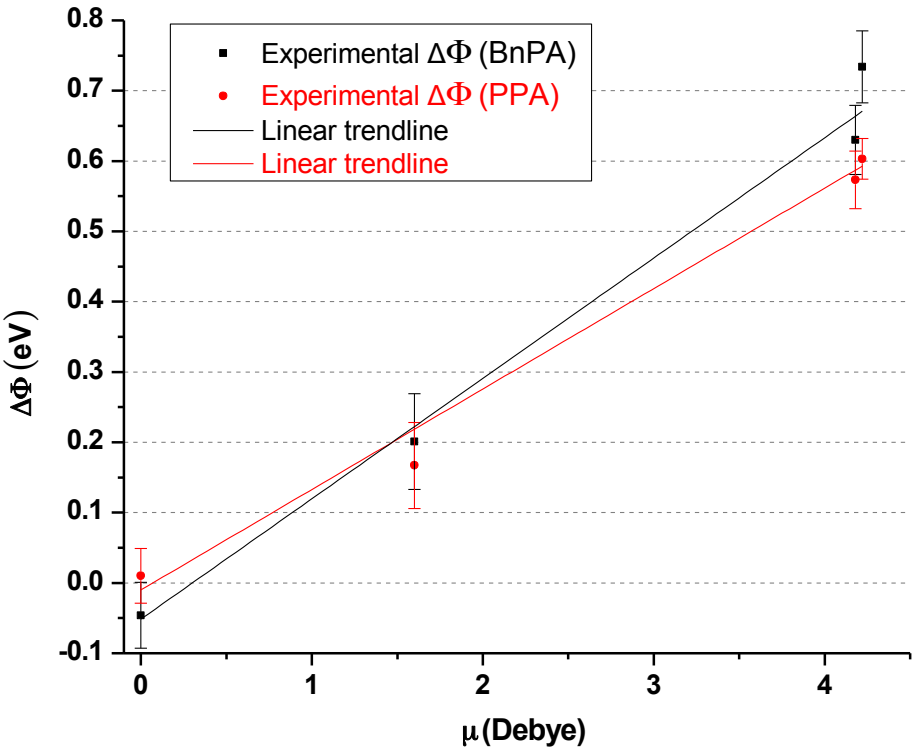
Here to plot the relationship between the work function changes and different functional groups on the benzylphosphonic acids, all the work function change values reported in Chapter 3 have been normalized to the value with the same coverage level of benzylphosphonic acid (which has the largest coverage density among the benzylphosphonic acids). Similarly, the work function values of the ITO surfaces modified by the phenylphosphonic acids have been normalized to the value with the same coverage level of phenylphosphonic acid (which also has the largest coverage density among the phenylphosphonic acids).

In terms of representing the properties of the functional group, the Hammett parameter α_p (obtained from Anslyn et al.[1]) of the corresponding substitution groups at the *para* position of the PA molecules as wells as the experimental dipole moment μ of the mono substituted benzene[2] of the corresponding PA molecules are used here, since they are both good indicators for the properties of the functional groups.

The relationship between the work function changes and the Hammett parameter α as well as the relationship between the work function changes and the dipole moment μ of the mono substituted benzene of phosphonic acids are compared respectively in the figure below. (Benzylphosphonic acids and phenylphosphonic acids are compared separately)



a) Comparison of the coverage-normalized work function changes of DSC/OP ITO measured by Kelvin Probe as a function of the Hammett parameter (α) of the functional group on the phosphonic acids



b) Comparison of the coverage-normalized work function changes of DSC/OP ITO measured by Kelvin Probe as a function of the dipole moment (μ) of the analogous mono substituted benzene of the corresponding phosphonic acids

Figure 4.1 Evolution comparisons

According to Figure 4.1 a) above, a linear correlation was found between the work function changes of ITO surfaces modified by different benzylphosphonic acids (phenylphosphonic acids) and Hammett parameter of the functional group at the *para* position on the corresponding benzylphosphonic acid (phenylphosphonic acids). The

slope of the linear trendline for benzylphosphonic acid and phenylphosphonic acids are 0.94 eV, 0.72 eV respectively. As obtained from Figure 4.1 b), the slope of the linear trendline for benzylphosphonic acid and phenylphosphonic acids are 0.17 eV/Debye, 0.14 eV/Debye respectively. These values can be compared with the work function change values reported in the literature[5] for other benzylphosphonic acids and can be plotted with the dipole moment of the analogous mono substituted benzene of the corresponding phosphonic acids. The phosphonic acids with reported absolute work function values are 2,6-difluorobenzylphosphonic acid, 4-fluoroben-zylphosphonic acid, 4-(trifluoromethyl)benzylphosphonic acid. The work function change values are obtained by setting the absolute work function value of 2,6-difluorobenzylphosphonic acid as zero and comparing to other work function values. The slope of the linear trendline was found to be 0.18 eV/Debye, which is consistent with the value we obtained for benzylphosphonic acids (0.17 eV/Debye).

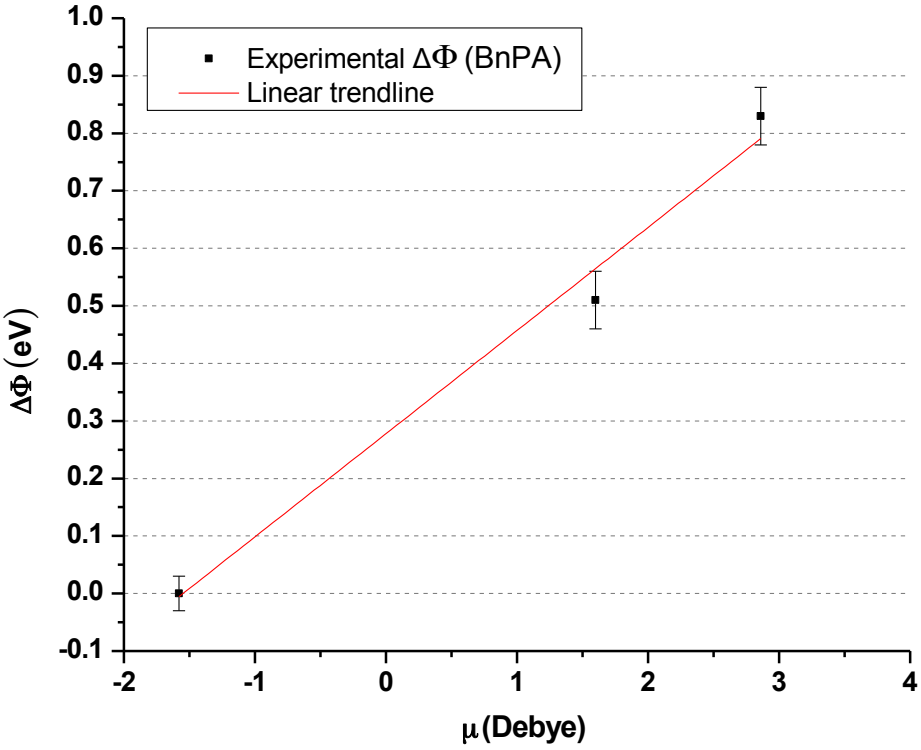


Figure 4.2 Comparison of the work function changes measured by Kelvin Probe as a function of the dipole moment (μ) of the analogous mono substituted benzene of the corresponding phosphonic acids.

It has been reported[6] that the bond dipole (BD) has a similar effect on the work function change regardless of what head group is on the phosphonic acid. The approximate linearity demonstrated above then suggests that the geometry rearrangement energy of the surface would not contribute significantly to the work function changes for different modifiers, but the magnitude of the dipole moment created upon attachment of the phosphonic acids onto the ITO surface has the largest influence on the work function changes. It is also interesting to note that a lager slope is observed for the benzylphosphonic acids, indicating that the modification of the work function of

benzylphosphonic acids is more sensitive to the head group changes than phenylphosphonic acids.

Similar studies have been reported, though using different surface modifiers and/or different surfaces and different x-axis parameters (i.e. the dipole moment normal to the surface created by adsorption of the phosphonic acids). The dipole moment was defined positive either toward the surface or outward the surface. Bruner *et al*.[3] reported a variation of the work function of ITO by attachment of substituted phenoxy–tin compounds on ITO. They found a good linear correlation between the dipole moment of the surface modifiers (in the gas phase) and the work function change ($\Delta\Phi$) of the ITO, resulting in a slope of -0.11 eV/Debye. Alloway *et al.*[4] found a linear correlation between the component of dipole moment of the modifiers normal to the surface and the changes in work function for a series of alkyl and semi–fluorinated alkylthiols on gold. They found a slope of -0.51 eV/Debye. Hotchkiss *et al.*[5] reported a slope of the experimental data (-0.48 eV/debye) for the work function evolution with the dipole moment of to the surface created by adsorption of a series of fluorobenzylphosphonic acids. Additionally the calculated data (-0.39 eV/Debye) they obtained is in good agreement with the experimental data.

Lastly, the overall work has achieved the goal of this specific research by judicious choosing of the surface modifiers, successful experiments and characterization of the chemicals and surfaces as well as the subsequent analysis of the characterization result. The conclusion provided in this chapter can be a good insight when choosing the surface modifier to alter the work function to the desired level.

4.1 References

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